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Dongqi Li
Syracuse University

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

M. Onellion
University of Wisconsin, Madison

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MULTIPLY FINE STRUCTURE OF THE Gd AND Tb 5P LEVELS

Dongqi Li and P.A.Dowben

Department of Physics, Syracuse University, Syracuse, NY 13244-1130

M.Onellion

Department of Physics, University of Wisconsin, Madison, WI 53706

ABSTRACT

Fine structure is observed in the photoemission of Gd and Tb 5p levels as a result of multiplet splitting. These splittings are the consequence of different J final states that occur as a result of interactions with partly filled 4f and/or 5d levels.

INTRODUCTION

Photoemission from shallow core levels has been employed to probe magnetic ordering[1-7]. Recently we have investigated the rare earth 5p levels in different photoemission geometries to study rare earth thin film magnetism[3,4]. A model for the photoemission shallow core level fine structure is important to the understanding of this measure of magnetic ordering, the p-level anisotropy[3].

Rare earth metals are well known for exhibiting pronounced multiplet splittings of the 4d levels[8-11], 4f levels[10, 12-15] and 4s and 5s levels[10, 16-17]. Here we report, for the first time, the multiplet splittings of the Gd and Tb 5p levels and provide an explanation for their origin. As expected, the 5p photoemission fine structure due to multiplet splittings is a result of the unfilled 4f and 5d levels. We have undertaken our preliminary analysis by considering 4f⁷ only for convenience. Contributions from the 5d levels would not be expected to affect the number of multiplets, though this may seriously affect the multiplet oscillator strengths.

EXPERIMENTAL

The angle resolved photoemission experiments were carried out on a system described elsewhere[2] on a 6m toroidal grating monochrometer at the Synchrotron Radiation Center in Stoughton, Wisconsin. The photoelectrons were collected normal to the surface. The incident light of 37 or 70 degrees off normal was used to provide larger portion of light with its vector potential parallel to or perpendicular to the thin film (s- or p- polarization respectively). The combined energy resolution for photoemission was 0.25 eV.

Gd and Tb were deposited at room temperature onto W(110) and Ni(111) substrates respectively. The methods for preparing clean rare earth films have been described previously[1,2]. For Gd/W(110), the base pressure was normally 7×10^{-11} torr and the maximum during the deposition was 2×10^{-10} torr, while for Tb/Ni(111), the pressure was less than 5×10^{-10} torr during the evaporation. The thickness was determined by a quartz crystal oscillator. The relative thickness has small error of <2% while the absolute value can only be taken as nominal thickness. 1-3 monolayer Gd films on W(110) show sharp LEED pattern indicating the epitaxial growth with (0001) orientation of the hexagonal Gd overlayer. Tb/Ni(111) films were not well-ordered.

RESULTS

Photoemission spectra of the Gd 5p features were taken at 50 eV and 60 eV for Gd films on W(110) of different thicknesses. Fig. 1a is one of the typical spectra which include two main features with binding energies of about 21 and 28 eV below the Fermi energy. For the films thicker than one monolayer, 21 eV photoemission feature exhibits fine structure as shown in Fig. 1a. The envelope can be fitted well with four Gaussian peaks with binding energies of 20.3 ± 0.1 eV, 20.9 ± 0.1 eV, 22.0 ± 0.2 eV, and 23.4 ± 0.3 eV (Fig. 2a). Gd valence band spectra (not shown here and discussed in detail elsewhere[18]) shows 5d bands at 0.2 ± 0.1 eV and 1.3 ± 0.1 eV. The 4f levels are observed at 8.6 ± 0.1 eV. It should be noted that the FWHM of the 4f is 1 eV and that of 5d about 0.5 eV.

The 5p levels of Tb/Ni(111) are shown in Fig. 1b. There are two main features with binding energies of 22 and 28 eV respectively. As with Gd, the lower binding energy feature contains several peaks. The binding energies of these fine structures are 20.7 eV, 21.6 eV, 22.7 eV, and 23.7 eV, as seen in Fig. 2b.

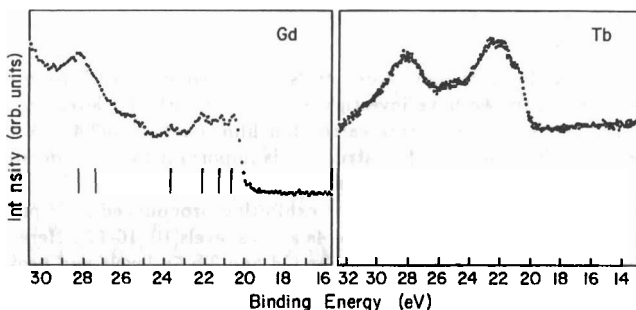


Fig. 1. (a) A typical Gd 5p level photoemission spectrum with photon energy of 50 eV. (b) Tb 5p level photoemission spectrum with the photon energy of 60 eV.

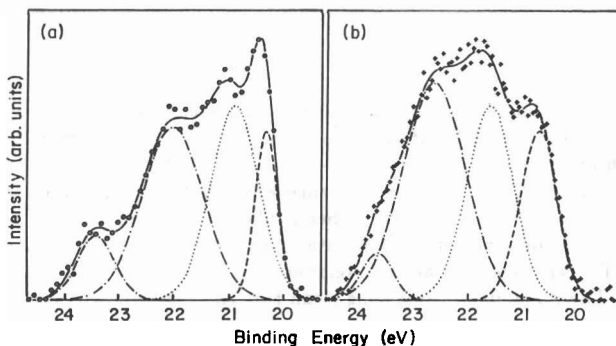


Fig. 2. The lower binding energy envelopes in Fig. 1. are fitted with four Gaussian functions after the linear background subtraction. The solid lines are the fitting result while the other lines showing the individual Gaussian function.

DISCUSSION

The large energy separation (~ 7 eV) of the two main features has been observed and is considered a result of spin-orbit coupling[10,19]. This value for the spin-orbit Gd

5p coupling is larger than the calculated result of 4.0 eV for atomic Gd[20]. Spin-orbit coupling only predicts two features, i.e. $5p_{1/2}$ and $5p_{3/2}$, without any further detailed structure.

Since rare earth atoms have unpaired 4f and 5d electrons, multiplet structures, caused by the interaction between the core level photohole and those partly filled subshell, can have a strong influence on the core level spectra. Multiplet structures can be understood as a final state effect in photoemission. After one 5p electron is excited, the hole left over will have an electrostatic interaction (direct, i.e. Coulomb interaction and indirect, i.e. exchange interaction) with the electrons in unfilled subshells to form different final states. This effect has been well studied on filled s and p core levels of some transition metals and rare earth 4s, 5s, and 4f levels[15-17, 21-23]. Most of multiplet studies have only considered the exchange interaction between the unpaired spins which results in two main features characterized by the hole spin parallel or anti-parallel to that of the unpaired electrons. Configuration interactions were proven to be an important addition to this simple picture[23-24] and may cause further splitting in photoemission spectra. For s-levels, there is no spin-orbit interaction since they have no orbital momentum ($l=0$). For p-levels ($l=1$), spin-orbit interaction can be ignored only when it is much weaker than the exchange interaction between the hole and other electrons, that is, in L-S coupling limit.

With L-S coupling scheme, we can work out the possible multiplets for Gd. The ground state configuration of Gd atom is $4f^7 5s^2 5p^6 5d^1$. Since $5d^1$ is mainly polarized by 4f electrons, here we only write down the coupling of 5p hole and $4f(^8S_{7/2})$ electrons for convenience. The existence of $5d^1$ electrons should not affect the basic result of the following discussion as indicated later in this paper. Photoemission of one 5p electron leaves an ion in $5p^6 4f^7$ configuration, which is complementary to $5p^1 4f^7$ (one 5p hole and seven 4f electrons). Since $l=1$, $s=1/2$ for 2P and $L'=0$, $S'=7/2$ for 8S , L-S coupling of $5p^1(^2P)$ and $4f^7(^8S)$ results in $^7P_{4,3,2}$ and $^9P_{3,4,5}$ final states with $L=L'+l$, $L'+l-1$, ... , $|L'-l|$, $S=S'+s$, $S'+s-1$, ... , $|S'-s|$ and $J=L+S$, $L+S-1$, ... , $|L-S|$. Without considering spin-orbit coupling, the two main features should be assigned as 7P and 9P with the later one at the lower binding energy. If weak spin-orbit coupling exists, the degeneracy of different J values should be lifted and 21 eV feature should split to three features of 9P_3 , 9P_4 , 9P_5 . Experimentally, we observe a four-fold splitting. Configuration interaction can cause further splitting of the photoemission features. Since 9P term can only come from one configuration with all the spins of 5p hole and 4f electrons parallel, 9P cannot further split and cannot exhibit fine structure beyond the three basic features. Since L-S theory predicts only three features and we observe four in our experiments (Fig.2), configuration interaction combined with L-S coupling scheme cannot be used to explain the observed data.

Alternatively, j-j coupling can also result in multiplet splitting. Gupta and Sen[25] considered spin-orbit coupling in their multiplet calculations of Mn^{2+} 2p and 3p levels and realized that spin-orbit coupling can be ignored for the Mn 3p levels but it is the major factor in determining the photoemission structure of the 2p levels. Their calculations are qualitatively confirmed by experiment[23]. In rare earth 5p levels, spin-orbit coupling is strong and is larger for the heavier rare earths than the light rare earths. With strong spin-orbit coupling, the two main features should be assigned as $5p_{1/2}$ - and $5p_{3/2}$ -based levels with the latter one at lower binding energy. The relatively weaker exchange interaction of 5p hole with 4f and 5d electrons will lift the J-degeneracy. The $j=3/2$ term couples with $^8S_{7/2}$ to form four terms of $(3/2, 7/2)_5$, $(3/2, 7/2)_4$, $(3/2, 7/2)_3$, and $(3/2, 7/2)_2$ since $J=J'+j$, $J'+j-1$, ... , $|J'-j|$. This is consistent with the four-fold splitting observed by

experiment. Since L-S coupling and j-J coupling should give out the same J-state energy order[26], we can assign the features with J quantum numbers as shown in Fig. 3. As Kowalczyk et al.[23] pointed out for Mn 2p levels, this splitting will result in an increase in the spin-orbit splitting, which could explain the increase of the splitting between the $5p_{1/2}$ and $5p_{3/2}$ levels (7 eV) compared with theoretical spin-orbit splitting calculation (4 eV).

Fig. 3. The order of different J-terms in L-S and j-J coupling schemes

Whether L-S coupling or j-J coupling occurs is totally dependent on the strength of different interactions. It is not surprising that most s-level multiplets fit L-S coupling multiplet theory very well. For p-levels($l=1$), Mn 2p levels are better explained by j-J coupling while the 3p levels, with weaker spin-orbit coupling, agrees with L-S coupling qualitatively[23, 25]. Considering the magnitude of the two energy splittings caused by the two kinds of interaction (about 7eV and 1eV in our experiment), it is likely that a coupling intermediate between L-S and j-J occurs in the case of Gd 5p multiplets.

Several other effects may also considered as the possible origin of the 5p fine structure. Possible chemical shift, multiple valences, shake up or shake off effects can cause splittings in valence bands as well as in core levels. The necessary kinds of splittings are not observed, however, for the valence band[18] excluding these effects as the source of the shallow 5p core level fine structure in photoemission. Surface to bulk core level shifts have been observed in Gd 4f level of 0.5 eV[12]. We can expect a similar magnitude of shift for the 5p levels. This effect cannot explain the energy separation of at least 0.7 eV between 5p fine structure features and the observation of four, instead of two features in the $5p_{3/2}$ photoemission envelope.

The existence of magnetic field can also cause the lifting of degeneracy in $5p_{3/2}$ and also forms four features with $m_j=3/2, 1/2, -1/2, -3/2$. This is, however, not likely to occur with a splitting as large as observed by experiment, nor can it explain the observed photoemission fine structure. This kind of magnetic field induced splitting should result in equal energy separations of $\Delta E=g\mu_B H$. This is not observed in the experimental results. Estimating the magnetic field necessary to produce an energy splitting shown in the experiments (~ 1 eV) with $\Delta E\sim\mu_B H$, we find $H\sim 10^8$ Gs. This is inconsistent with any reasonable external field produced by the rare earth film. If the field is produced by a magnetic dipole, the mean distance between the dipole and 5p electron should be about 10^{-10} cm. This is much smaller than the average distance between 4f and 5p or 5d and 5p electrons. Thus the local magnetic field produced by 4f and 5d magnetic moments cannot result in the observed photoemission fine structure of the rare earth 5p levels.

Possible crystal field effects has also been considered. Since Gd films show hexagonal structure, we treat $5p_{1/2}$ and $5p_{3/2}$ levels with a crystal double group based on D_6 point group(D_6') (Table I) similar to those derived by Tinkham[27] for cubic crystal. Comparing the character values of $p_{1/2}$ and $p_{3/2}$ levels with D_6' character table, we get $p_{1/2} \rightarrow E_3$

$$p_{3/2} \longrightarrow E_3 + E_5$$

This means that $5p_{1/2}$ should not split while $5p_{3/2}$ should split to two features. This effect itself cannot explain the four-fold splitting. Furthermore, since crystal field effect is basically electrostatic interaction caused by a periodically distributed charge density, it should be stronger for the outer levels. However, Gd 5d feature has only FWHM of 0.5 eV at normal emission. We conclude that crystal field effects do not play an important role in determining rare earth 5p fine structure, although we cannot eliminate crystal field contribution completely.

Table I. The character table of the crystal double group D'_6 (the first 9 lines) and the corresponding characters of the rotation groups D_J with $J=1/2$ and $J=3/2$ (the last 2 lines).

D'_6	E	R	C_2+RC_2	$2C_3$	$2RC_3$	$2C_6$	$2RC_6$	$3C'_2+3RC'_2$	$3C''_2+3RC''_2$
irreducible representations of D'_6	A_1	1	1	1	1	1	1	1	1
	A_2	1	1	1	1	1	1	-1	-1
	B_1	1	1	-1	1	1	-1	1	1
	B_2	1	1	-1	1	1	-1	-1	-1
	E_1	2	2	-2	-1	1	1	0	0
	E_2	2	2	2	-1	-1	-1	0	0
	E_3	2	-2	0	1	-1	$\sqrt{3}$ $-\sqrt{3}$	0	0
	E_4	2	-2	0	1	-1	$-\sqrt{3}$ $\sqrt{3}$	0	0
	E_5	2	-2	0	-2	2	0	0	0
$j=1/2$	2	-2	0	1	-1	$\sqrt{3}$ $-\sqrt{3}$	0	0	0
$j=3/2$	4	-4	0	-1	1	$\sqrt{3}$ $-\sqrt{3}$	0	0	0

It should be noted that although we did not consider 5d¹ electron in our multiplet analysis while writing out the final state terms, it is likely that 5d electrons have large contribution to 5p multiplets since they have the same principle quantum number. The j-J coupling of 5d¹(²D_{5/2}) and 5p¹(²P_{3/2}) results in four terms of J=4, 3, 2, and 1, which is also correspond to a four-fold splitting as we consider the coupling with 4f only. Further experiments and detailed calculations are needed to determine the portion of 5d contribution.

Tb has ground state configuration of 4f⁸5s²5p⁶5d¹. This is similar to that of Gd though Tb has only six unpaired 4f electrons instead of seven in Gd. Most of the above discussion is valid for Tb. The fine structure can again be explained as multiplets under j-J coupling or intermediate coupling scheme.

CONCLUSION

We have observed the photoemission fine structure splitting the 5p levels for Gd and Tb. Our analysis suggests that multiplet structures arise as result of j-J coupling or intermediate coupling scheme. Since j-J coupling is more complicated than L-S coupling, more theoretical calculations considering spin-orbit coupling, exchange interaction, configuration interaction, and crystal field effects are necessary to fully understand this effect. Since the fine structure is caused by exchange interaction of the unpaired electrons, it has the potential to be used to study rare earth 4f and 5d unpaired spins and may give us some insights to many interesting problems such as local spin and mixed valence.

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REFERENCES

1. D.LaGrafte, P.A.Dowben, and M.Onellion, Phys. Rev. B40, 970 (1989).
2. P.A.Dowben, D.LaGrafte, and M.Onellion, J. Phys. Cond. Matt., 1, 6751 (1989).
3. D.LaGrafte, P.A.Dowben, and M.Onellion, Phys. Lett. A147, 240 (1990).
4. P.A.Dowben, D.LaGrafte, Dongqi Li, A.Miller, Ling Zhang, L.Dottl, and M.Onellion, Phys. Rev. B43, 3171 (1991).
5. C.S.Fadley, in *Magnetic Properties of Low Dimensional Systems II*, Springer Proceeding in Physics, vol.50, Edited by L.M.Falicov, F.Meija-Lira, and J.L.Moran-lopez, (Springer-Verlag, Berlin, 1990), p.36; Physica Scripta T17, 39 (1987).
6. B.Sinkovic and C.S.Fadley, Phys. Rev. B31, 4665 (1985).
7. B.Sinkovic, B.Hermsmeier and C.S.Fadley, Phys. Rev. Lett., 55, 1227 (1985).
8. C.S.Fadley and D.A.Shirley, Phys. Rev. A2, 1109 (1970).
9. S.P.Kowalczyk, N.Edelstein, F.R.McFeely, L.Ley and D.A.Shirley, Chem. Phys. Lett., 29, 491 (1974).
10. B.D.Padalia, W.C.Lang, P.R.Norris, L.M.Watson, and D.J.Fabian, Proc. R. Soc. Lond., 354, 269 (1977).
11. J.L.Dehmer, A.F.Starace, U.Fano, J.Sugar, and J.W.Cooper, Phys. Rev. Lett., 26, 1521 (1971).
12. R.Kammerer, J.Barth, F.Gerken, A.Flodström and L.I.Johansson, Solid State Commun., 41, 435 (1982).
13. Y.Baer and G.Busch, J. Electron. Spectrosc. Rel. Phenom., 5, 611 (1974).
14. J.K.Lang, Y.Baer and P.A.Cox, J. Phys. F11, 121 (1981).
15. P.A.Cox, J.K.Lang and Y.Baer, J. Phys. F11, 113 (1981).
16. R.L.Cohen, G.K.Wertheim, A.Rosenewaig and H.J.Guggenheim, Phys. Rev. B5, 1037 (1972).
17. F.R.McFeely, S.P.Kowalczyk, L.Ley and D.A.Shirley, Phys. Lett. 49A, 301 (1974).
18. Dongqi Li, C.Hutchings, P.A.Dowben, Rong-Tzong Wu, C.Hwang, M.Onellion, B.Andrews and J.L.Erskine, in preparation.
19. G.K.Wertheim, R.L.Cohen, A.Rosenewaig, H.J.Guggenheim, in *Electron Spectroscopy*, Edited by D.A.Shirley (Amsterdam: North Holland, 1972), p.813.
20. F.Herman and S.Skillman, *Atomic Calculations*, (Prentice-Hall, Englewood Cliffs, N.J., 1963).
21. C.S.Fadley, D.A.Shirley, A.J.Freeman, P.S.Bagus, J.V.Mallow, Phys. Rev. Lett., 23, 1397 (1969).
22. B.Hermsmeier, C.S.Fadley, M.O.Krause, J.Jimenez-Mier, P.Gerard, S.T.Manson, Phys. Rev. Lett., 61, 2592 (1988).
23. S.P.Kowalczyk, L.Ley, F.R.McFeely and D.A.Shirley, Phys. Rev. B11, 1721 (1975).
24. P.S.Bagus, A.J.Freeman and F.Sasaki, Phys. Rev. Lett., 30, 850 (1973).
25. R.P.Gupta and S.K.Sen, Phys. Rev. B10, 71 (1974); Phys. Rev. B12, 15 (1975).
26. H.E.White, *Introduction to Atomic Spectra*, (McGraw-Hill Book Company, 1934).
27. M.Tinkham, *Group Theory and Quantum Mechanics*, (McGraw-Hill Publishing Company, 1964), p.77.